

# *In Situ* Chemical Oxidation (ISCO): Current Advancement

Stephen Rosansky, P.E.

Abraham Chen, Ph.D., P.E.

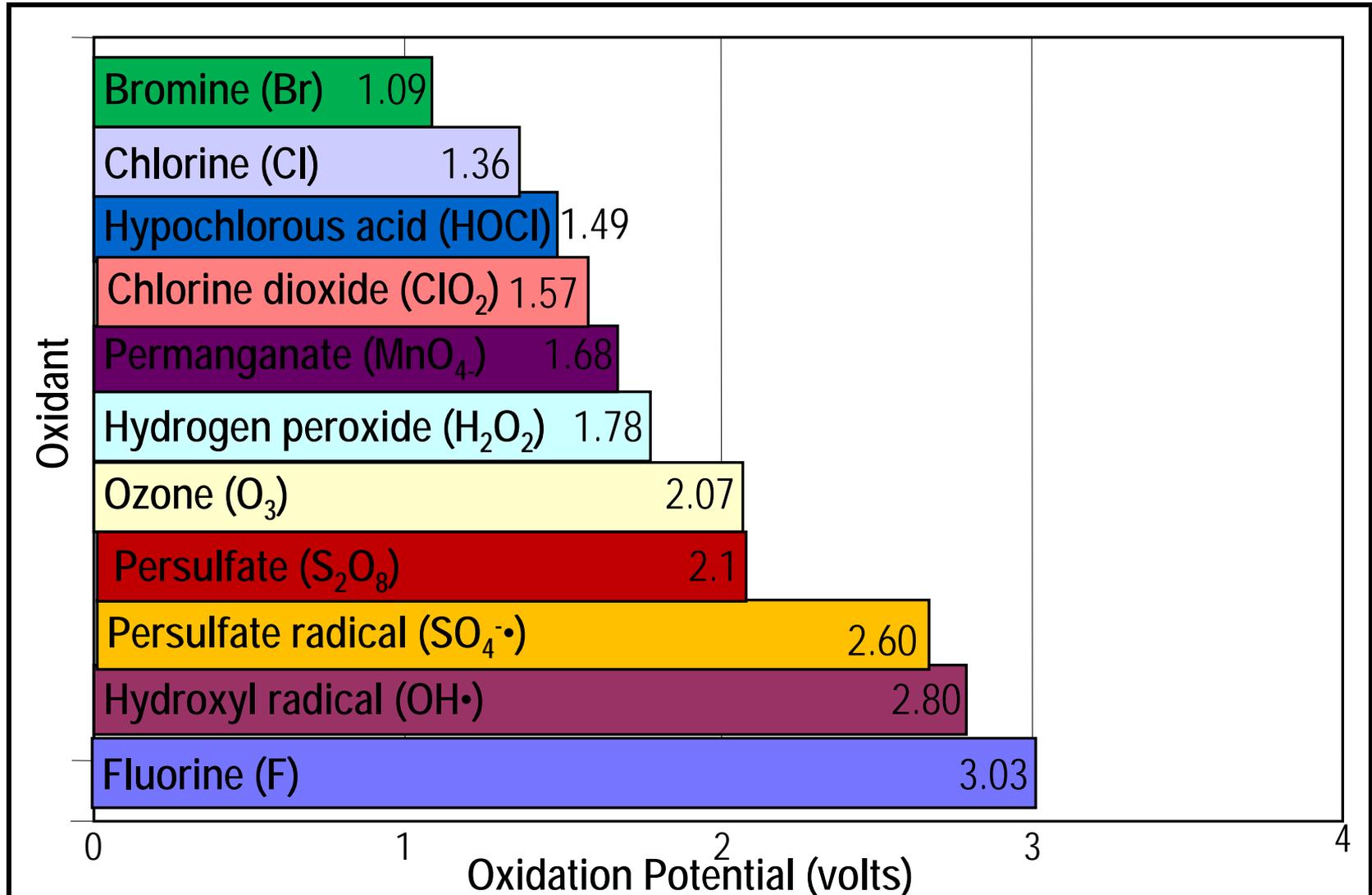
December, 2009

# Principles of Common Oxidation Processes

An oxidant is a chemical that has a tendency to accept electrons from other chemicals (preferably target contaminants in groundwater and soil)

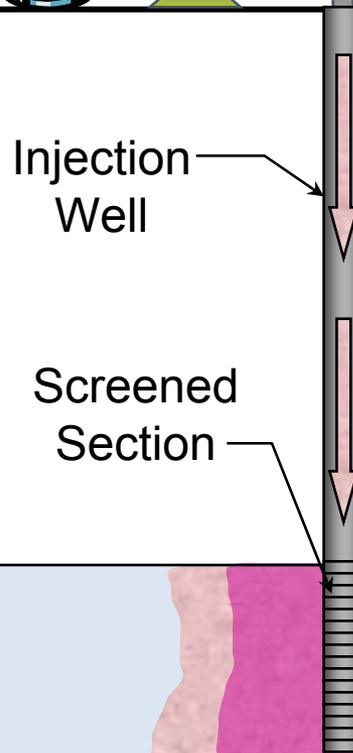
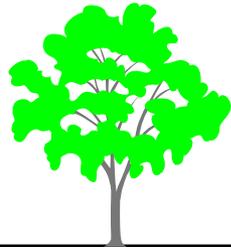
- The target contaminant is oxidized (loses electrons) and is transformed to a non-toxic or less-toxic product
- Oxidation potential is a measure of the oxidative power of an oxidant. The higher the oxidation potential (volts), the greater the oxidative power.

# Oxidation Potential of Select Oxidants



# ISCO Conceptual Injection Process

*Reagent is injected and occupies set volume*



$MnO_4$   
 $H_2O_2$   
 $S_2O_8$

Spread of Reagent

Residual DNAPL

Monitoring Well

Water Table

Contaminated Aquifer

Groundwater Flow Direction →

# ISCO Definitions

- Can be used to treat dense, nonaqueous-phase liquid (DNAPLs) as well as dissolved-phase contaminants
- Does not rely on biological processes
- May not require aboveground treatment, as with pump and treat (P&T) systems, thermal heating, and surfactant flushing

# Advantages and Limitations

- Advantages

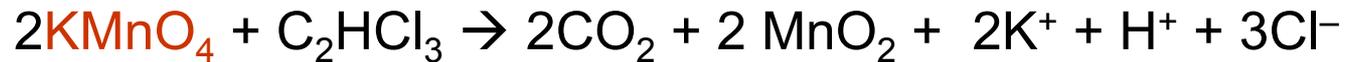
- Can destroy contaminants *in situ* (unlike thermal or surfactant flushing technologies)
- Reagents relatively inexpensive (e.g.,  $\text{KMnO}_4$  at \$1 to \$1.50/lb)
- Is potentially effective with many different types of organic contaminants in sorbed and DNAPL states
- Is cost-effective for contaminant source zones or "hot spots"

- Limitations

- Has some handling hazard (e.g., hydrogen peroxide)
- As with any in-situ technology, reagent delivery to the target regions may be challenging
- Strong oxidants may oxidize other (naturally occurring) reduced species in the subsurface
- An injection permit may be required
- May not be cost-effective for treating very dispersed, dilute contamination (i.e., dispersed contaminant plume)

# Common Oxidant Chemistries

- Permanganate oxidation



- Fenton's Reagent



- Persulfate



# Permanganate – Target Contaminants

- Permanganate has been shown to oxidize:
  - Chloroethenes (e.g., TCE)
  - PAHs
  - Chlorinated pesticides (e.g., aldrin and dieldrin)
  - High explosives
  - Some chlorophenols
- Permanganate is ineffective with:
  - Chlorinated alkanes (e.g., TCA, dichloroethane)
  - Aromatic hydrocarbons (e.g., benzene and chlorobenzene)
- MTBE – is oxidized to TBA
  - Functional group is oxidized, but not the parent structure

# Permanganate Reagents

- Sodium permanganate
  - Supplied as dark purple liquid (40% min. conc.)
  - No concerns with dust
  - More expensive than  $\text{KMnO}_4$
- Potassium permanganate
  - Supplied as crystalline solids
  - Mixed onsite
  - Concerns with dust
  - Derived from mined potassium ores; hence contains small amounts of impurities, such as metals,  $^{40}\text{K}$ , etc.



**$\text{KMnO}_4$  Solution**

# Factors Affecting Permanganate Application

- Soil oxidation demand (SOD) often exceeds the oxidant demand of the COC, sometimes by 2 or 3 orders of magnitude
  - **Reduced solid species (e.g., sulfides, ferrous iron minerals, etc.)**
  - **Natural organic matter**
  - **Aqueous species (dissolved iron, etc.)**
- **Near potential receptor (purple water)**

# Advantages and Limitations: Fenton's Reagent

- **Advantages**

- Hydroxyl free radical is much more reactive than permanganate and can therefore oxidize many more COCs
- Reactions that generate multiple free radicals destroy nearly all organic contaminants
- Ability to treat strongly sorbed and DNAPL contaminants
- Chemicals involved do not appear to contain trace impurities of concern
- Color is not a concern
- No significant generation of solids that could clog the aquifer

- **Limitations**

- Peroxide and hydroxyl free radicals are extremely short-lived and this could limit distribution (reaction rate is diffusion controlled). Other reactive species generated are more long-lived.
- Safety issues with H<sub>2</sub>O<sub>2</sub>
  - ✓ **Chemical fires and explosions**
  - ✓ **Chemical burns**
- ✓ Reaction is highly exothermic and higher peroxide concentrations can cause steaming and volatilization of COCs

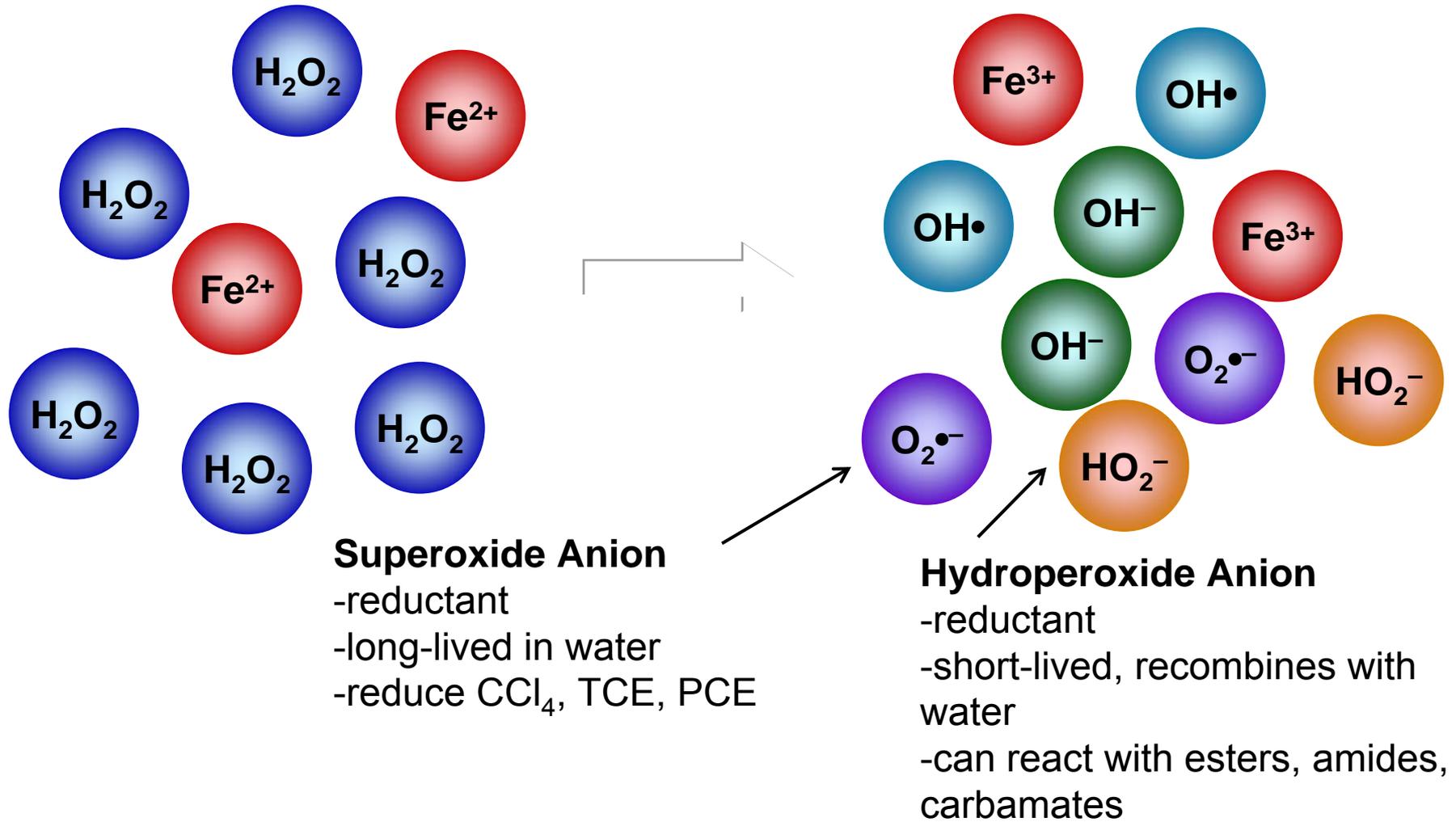
# Compounds Not Reactive with Hydroxyl Radicals (OH•)

- Halogenated Alkanes
  - Carbon tetrachloride
  - Hexachloroethane
  - Chloroform

# Modified Fenton's Reagent Applications

- Use of relatively high hydrogen peroxide concentrations  
(typically 2%-12% H<sub>2</sub>O<sub>2</sub>)
- A range of different materials can catalyze the generation of free hydroxyl and other reactive radicals
  - Soluble Iron (II): Most common so far, with the addition of FeSO<sub>4</sub>
  - Iron (III)
  - Naturally occurring minerals
  - Iron chelates

# Modified Fenton's Reagent: Formation of Other Reactive Species



# Catalysis by Iron Chelates

- Iron-EDTA (Ethylenediaminetetraacetic Acid)
- Iron-NTA (Nitrilotriacetic Acid)
- Iron-Citrate

## Advantage:

- Promote Fenton's reactions at neutral pH

## Disadvantages:

- High potential for metals mobility
- Chelate is oxidized

# Catalysis by Iron Minerals

- Natural soil minerals can catalyze the reaction and form reactive radicals
- At many sites, there may not be a need to add ferrous compounds
- pH 3 to 4 required (acid addition)
- pH rebounds after treatment
- Releases carbonates as  $\text{CO}_2$
- Provides highest degree of  $\text{H}_2\text{O}_2$  stability
- Addition of an iron catalyst not required

# Factors Affecting Fenton's Reagent Application – Presence of COCs as DNAPL

- Evidence from the field has indicated DNAPL destruction by Fenton's reagent
- DNAPL destruction by Fenton's reagent has been documented through laboratory research and occurs more rapidly than any other treatment process (up to 50x the rate of natural dissolution)
- DNAPL destruction most likely does not involve hydroxyl radicals, but is likely superoxide
- Even when dissolved COC concentrations do not show a significant decrease, considerable DNAPL mass may have been oxidized
  - Exothermic reaction may cause higher desorption
  - DNAPL destruction may cause improved advective flow and higher dissolved concentrations

# Peroxide Distribution and Dosing

- Peroxide instability limits distribution
  - Primary catalysts for the unproductive decomposition of hydrogen peroxide in subsurface are manganese oxides
- Formation of large volume of vapor

**Implication:** Treatability tests should be conducted to monitor peroxide decomposition rates, and therefore, the well spacing, need for vapor recovery, etc.



**Gas in Monitoring Well during Fenton's Application**

# Peroxide Distribution and Dosing (Cont.)

- Optimum hydrogen peroxide concentrations are usually 0.5%-12% and are highly site specific
  - Lower concentrations (0.5%-1%) are most effective when contaminants are not sorbed and DNAPLS are not present
  - Higher concentrations (2%-12%) are usually required to treat sorbed and DNAPL contaminants
  - Concentrations >12% are problematic because of highly exothermic reactions and rapid decomposition of hydrogen peroxide

# Advantages and Limitations of Persulfate

- Advantages

- Sulfate free radical is much more reactive than permanganate and can therefore oxidize many more COCs
- Less oxidant demand than permanganate
- More stable than the hydroxyl free radical
- Ability to treat strongly adsorbed and DNAPL contaminants
- Color is not a concern
- Minimal safety issues (primarily dust)

- Limitations

- Requires on site mixing
- As with all oxidants, application can mobilize metals
- Newer, less understood than other reagents
- Forms sulfuric acid, can lower aquifer pH
- May degrade soft metals (copper, brass)
- Requires an activation agent for best results

# Available Forms of Persulfate

- Ammonium persulfate
- Potassium persulfate
  - Limited solubility in water (6%)
- Sodium persulfate
  - Most commonly used
  - Supplied as crystalline yellow solid, mixed on site
  - Relatively high solubility in water (40%)

# Persulfate Activation Methods

- Iron
  - Requires low pH or chelating agent (similar to Fenton's)
  - Efficiency decays with time and distance from injection
  - Optimum loading of 100 to 250 mg/L
  - May not need to add at some sites
- Heat (steam or resistive heating)
- Alkaline (pH >10)
  - sodium hydroxide
  - Shown to oxidize chloromethane, chloroform, and TCA
- Hydrogen peroxide

# Reagent Application Methods

- Direct injection - The reagents are injected directly into the subsurface in a specified volume of water from an external source, displacing groundwater corresponding to the volume of reagent injected
- Pull-Push: A set volume of groundwater is extracted, amended with reagents above ground and then reinjected into the subsurface through the same well
- Recirculation: In a closed system, groundwater is extracted from a set of extraction wells, amended with the reagents and then reinjected into a different series of injection wells.

**Multiple injections may be required!!!**

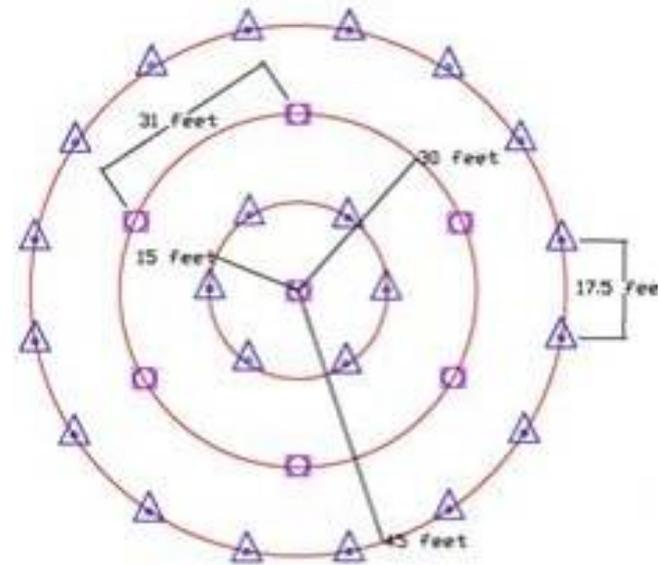
# Oxidant Application - Direct Injection

- Injection Only (currently more practiced, viewed as "easy")
- Injection wells have to be arranged in a way that makes use of natural gradient to distribute the oxidant
- Or, use multiple temporary injection points to inject the oxidant in several locations and depths in the target treatment zone
- Higher injection pressures may be required in tighter soils (possibility of spreading the COCs)
- Mn (discoloration) and trace metals could migrate downgradient

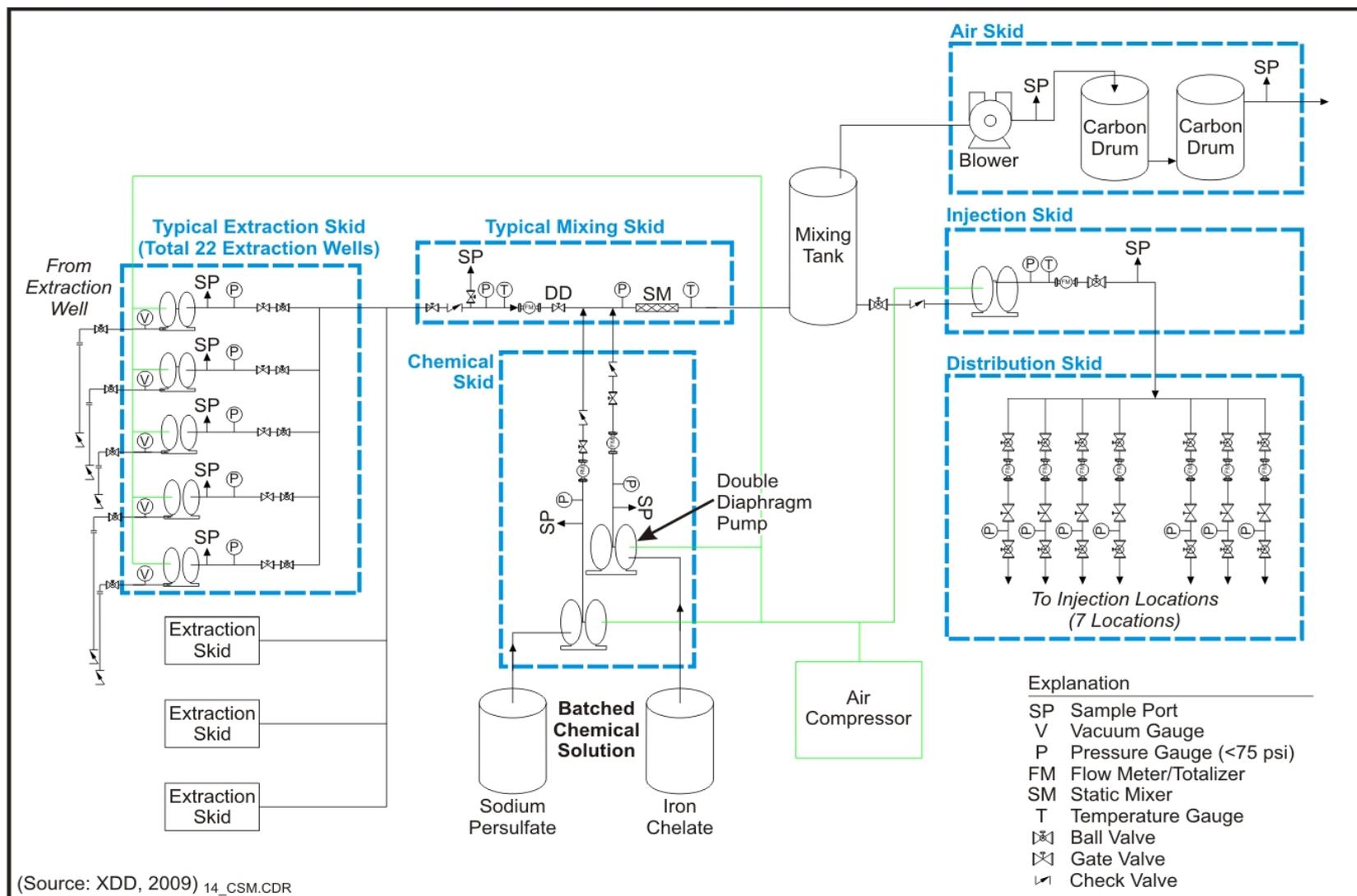


# Oxidant Application - Recirculation

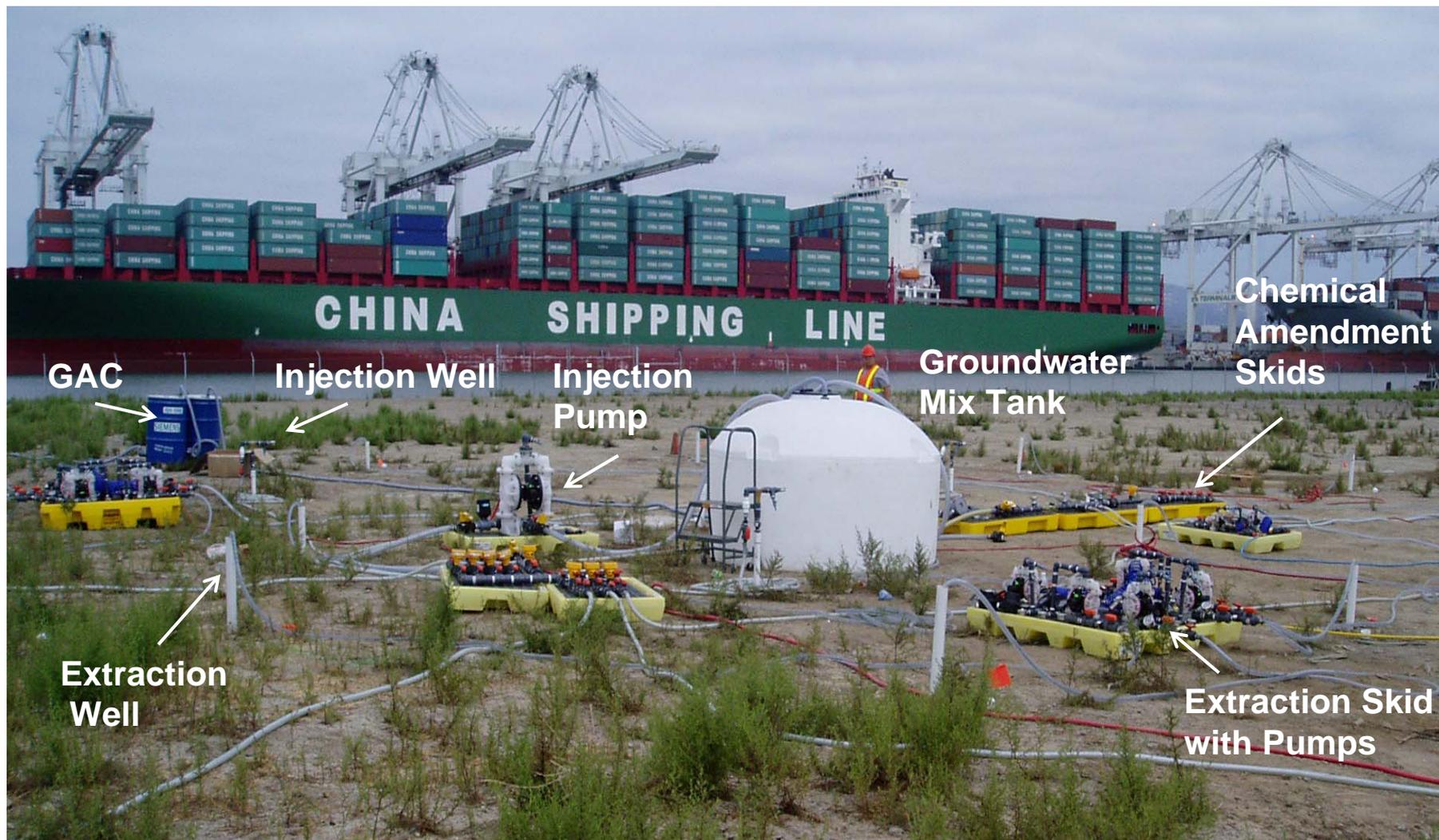
- Better hydraulic control – better distribution of oxidant, less chance of COC migration
- Reinjection may need to meet stricter guidelines
- More elaborate aboveground equipment required
- Typically lower oxidant dosing
- Minimizes potential for surfacing



# PID Drawing ISCO System



# Example System Layout



# Health and Safety Considerations

- Most safety concerns associated with application of hydrogen peroxide
- Proper personal protective equipment, including face shields, glasses, Tyvek® aprons, reinforced-toed boots, hard hats, are worn while working in the work zone
- Chemical oxidants must be stored within secondary containment pads
- Carefully monitor temperatures and pressures
- Injections discontinued if surfacing of reagents (“daylighting”) occurs
- Seals equipped with pressure relief valves installed on all injection points and monitoring wells to control release of fluids from wells



# Process Monitoring

- Performed during application
- Injection pressures, flowrates, and temperatures
- Groundwater quality parameters (very useful)
- Reagent levels in monitoring wells and extracted and injected water using real time analytical techniques
- Aboveground destruction of ethenes (in the case of recirculation)

Target Area	Volume Extracted <sup>(a)</sup>		Volume Injected <sup>(b,c)</sup>	Sodium Persulfate			Activator Solution <sup>(b,e)</sup>
	Volume (gal)	% Pore Volume <sup>(f)</sup> (gal)		Volume solution <sup>(d)</sup> (gal)	Mass (lbs)	Conc. (g/L)	
1	60,400	60	63,700	2,600	6,600	12	727
2	34,600	46	38,500	3,060	6,600	21	839
3	41,800	41	45,000	2,440	6,600	18	782
<b>Totals</b>	<b>136,800</b>		<b>147,200</b>	<b>8,100</b>	<b>19,800</b>		<b>2,348</b>

# Performance Monitoring

- Performed after concluding reagent injections
- May be performed quarterly or semi-annually
- VOCs and metals
- Groundwater quality measurements (pH, ORP, DO, temperature, and conductivity)
  - Is aquifer geochemistry returning to baseline conditions?
- Groundwater levels

